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STUDIES OF HETEROFACE SOLAR CELL PERFORMANCE

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1. Fabrication of $Al_xGa_{1-x}As$-GaAs Heteroface Solar Cells

1.1 Improvement in the Growth Technique

The growth system modifications noted in the last report did not result
in acceptably smooth succeeding grown layers. Experiments were done to iden-
tify the causes of non-smooth growth. Three distinct types of growth fail-
ure were apparent, all due to some kind of degradation of the substrate sur-
face. Therefore, even if a continuous aluminum-gallium arsenide layer is
formed, good solar cell performance cannot be expected from a non-smooth sam-
ple because of the importance of the substrate gallium arsenide in the opera-
tion of the desired structure.

The first type of failure is a many-micron deep furrowed, or "worm track",
appearance which is somewhat smoothed over by the aluminum-gallium arsenide
layer. When the layer is removed by etching in hydrochloric acid, the features
of the substrate are sharper. A temperature program in which the seed is
brought into contact with the melt ten minutes before the furnace is cooled
for growth,which was adopted to improve the quality of the heterointerface,may
be the cause. It is postulated that instabilities in the furnace temperature
during the time when the melt is in contact with the seed may result in non-
uniform etch back. Changing the temperature program by cooling the melt by
one degree before bringing the seed into contact and continuing to cool the
furnace has eliminated this problem,but may not give as good an interface.
Reducing the temperature of growth, from 950°C to 850°C or 800°C, should re-
duce the amount of arsenic lost from the substrate surface and tend to counter-
act the elimination of the cleaning period (melt in contact with substrate be-
fore growth to remove arsenic deficient surface layers).

The second failure mode is a very fine roughness, less than one micron deep, in the substrate surface. This appears to have been caused by a defective growth tube since replacing the tube has cured the problem. The growth tubes are quartz and tend to devitrify after extensive operation at high temperatures. They can leak at growth temperatures but not at room temperature. This leakage is not detectable with a helium mass spectrometer leak detector since the helium will diffuse through the wall of a sound quartz tube at the growth temperature.

The third type of failure is one that has appeared at random as long as the program of research has been in operation. It has the appearance of very deep scratches in the substrate surface, obviously caused by the substrate rubbing the top lamination of the boat. The scratches may be widely separated or crowded together so no undamaged surface appears between them. The latter behavior is usually seen at a high spot on the substrate surface, created by etching the substrate for many minutes in the cleaning procedure. Growth of aluminum-gallium arsenide does not usually cover scratches, especially when they are crowded together.

A recent growth run with scratches all the way across the substrate but with an aluminum-gallium arsenide layer on only three quarters of the region suggests that the scratches were made when the substrate was loaded into the boat and were enhanced by evaporation of arsenic as the furnace was heated. The scratches on the uncovered part of the substrate, although several micrometers deep, have smooth rounded walls and intersect rectangular pits filled with gallium along their length (no melt was in contact with this part of the surface). The rectangular pits are also seen around the edges of the substrate, where evaporation of arsenic is expected. The original scratches were not visible in the glove box when the substrate was examined after loading.

New boat components were fabricated from boron nitride (Union Carbide Corporation) in an attempt to alleviate the scratching problem. Boron nitride is chemically inert at our growth temperatures and has the advantage of being easier to machine than vitreous carbon. A slider and top lamination were made from boron nitride and used in several growth runs. It was found that the pockets for the seed and source crystals in the slider could be milled with much flatter bottoms than with vitreous carbon, although there was a tendency for the material to break off in laminar pieces from the narrow ridge between the pockets and the side of the slider. This breakage does not affect the operation of the boat.

Along with the better control and uniformity of pocket depths in the slider, it was hoped that boron nitride would make a top lamination that was less brittle and therefore less prone to crumble at the edge of the melt hole. The boron nitride top lamination did not give better results than the one made of carbon since the places where the seed rubbed against the top lamination still had a few scratches and rough growth. The old carbon top lamination was put back and the boron nitride slider retained.

Another approach to the scratch problem was a reduction in the maximum temperature during the growth cycle, although this was primarily done in an attempt to improve the current-voltage characteristics of our cells. A reduction in maximum temperature has two benefits: first, it allows a wider gap between the seed surface and the top lamination without degradation of the surface from arsenic loss, and second, it causes less widening of existing scratches. Both effects are due to the lowering of the equilibrium arsenic vapor pressure over the seed with the lowering of temperature. The scratch problem was not entirely eliminated by lowering the growth temperature.

The growth procedure as shown schematically in Fig. 1 has been modified slightly since the last time it was described in a status report. The gallium for the melt is baked in a separate carbon crucible immediately before the growth run. Only the gallium is baked, since at growth temperatures below 900°C no extra pieces of gallium arsenide are necessary to insure saturation of the melt. The crucible is necessary because the source crystal is now loaded at the same time as the seed to avoid partial evaporation of the source crystal during the gallium bake. The seed is loaded through the right-hand opening to reduce the possibility of scratching the seed surface.

1.2 Zinc Diffusion Depth Measurements

Studies of the diffusion of zinc into the GaAs to form the p-n junction indicate that the zinc diffuses primarily during the heatup time of the boat prior to the growth. Run 88A (Status Report, 4/16/73-10/15/73) was done to conclusively demonstrate this fact. In that experiment a melt and seed were loaded and the furnace heated to 850°C and held there for 15 minutes without the seed coming into contact with the melt. A junction depth of 0.83 microns was measured with the SEM, see Table 1. The results of other junction depth measurements done since then are summarized in Table 1. Although the time and temperature cycles of the growths vary considerably, it is possible to see expected effects between two runs where only one parameter varied between the runs. For instance, the junction depth in run 156 is about one-half of that of run 154, for a zinc concentration which was approximately halved.

The experience represented by Table 1 shows that it is possible to control the junction depth down to a value of about 0.5 microns, but below this level control is difficult. This reflects both the fact that the true junction depth depends on the zinc concentration profile and the substrate doping level and a difficulty in accurately measuring distances below 0.5 microns with our SEM.
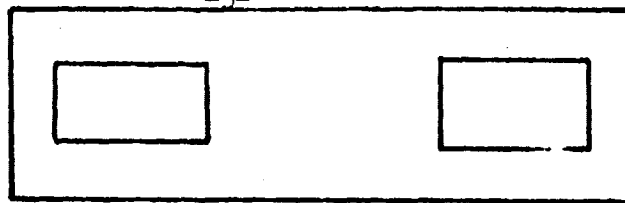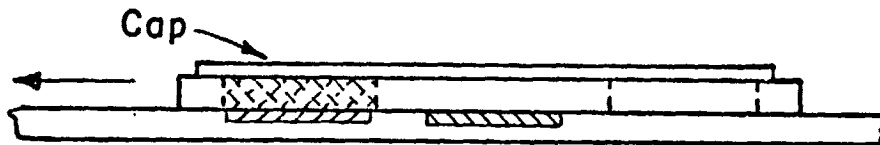
. Top View
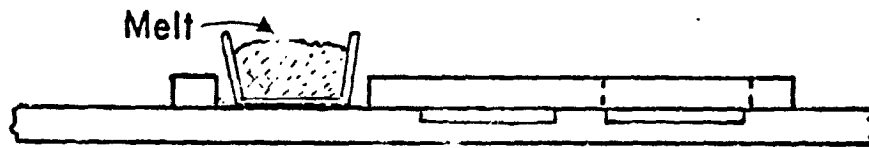
Melt

(1) Load Ga in crucible and bake with boat at 1000°C.
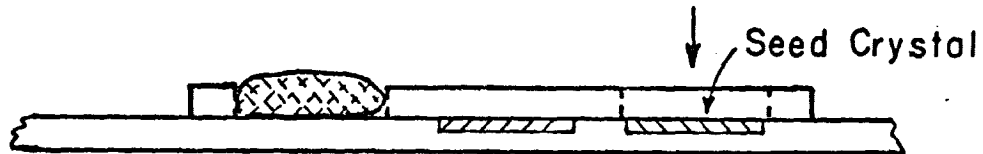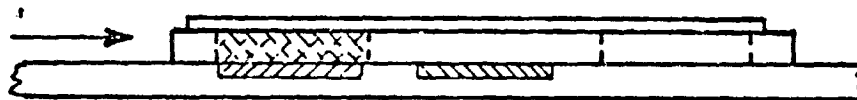
Seed Crystal

(2) Load Source Crystal Ga, Zn, Al; Load seed through right hand opening.

Cap

(3) Heat to 850°C for 15 min; cool to 800°C at 10°C/min with seed covered by carbon.
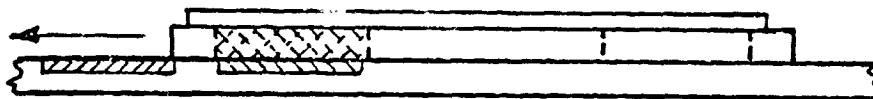
(4) Move slider at 800°C so seed is below melt and cool at 10°C/min to 797°C.

(5) Terminate growth by moving slider in reverse direction; open furnace.

Fig. 1 Schematic diagram of growth procedure

Table 1. Zn Diffusion Depth Measurements in Heteroface Solar Cells

Run	Substrate No. (cm^{-3})	Zn/Ga wt. ratio	Max.Temp. (°K)	Time at T_{max} (min)	Diffusion Depth (μm)
88A	2.5×10^{16}	-	1123	16	0.83
137	5×10^{17}	1.81×10^{-4}	1225	40	0
151	3×10^{16}	2.14×10^{-4}	1123	12	0.24
154	2×10^{17}	2.19×10^{-3}	1174	12	0.7
156	3×10^{17}	1.29×10^{-3}	1174	12	0.56
157	3.5×10^{17}	1.04×10^{-3}	1174	12	0.61
158	1×10^{17}	1.42×10^{-3}	1174	12	0.61
160	8×10^{16}	1.46×10^{-3}	1174	12	0.89
161	8×10^{16}	5.45×10^{-3}	1123	20	1.0
162	1×10^{17}	2.91×10^{-3}	1123	20	0.87
164	7.5×10^{14}	2.91×10^{-3}	1123	20	1.30
165	6×10^{14}	2.91×10^{-3}	1123	20	1.47
166	5×10^{16}	2.74×10^{-3}	1123	20	0.98

1.3 Ohmic Contacts

The procedure for making an ohmic contact to the front, or aluminum-gallium arsenide, side of the cell by evaporation of zinc followed by evaporation of silver and heating, has resulted in poor cell performance. The heating required to form the contact results in diffusion of silver into the junction region of cells with thin (a micron or less) aluminum-gallium arsenide layers. Cells with this kind of contact have a uniformly low performance as first noticed by H. Hovel of IBM. According to a paper by Boltaks and Shishiyanu, (translated in Soviet Physics-Solid State, Vol. 5, p. 1680), the rapid diffusion coefficient D for silver in gallium arsenide at 550°C is 5×10^{-7} cm^2/sec. Thus, a heat treatment of ten minutes gives a D·t product whose square root is ten microns. Silver is therefore seen to be nearly as bad as gold for use as a contact metal where any heating of the device takes place after the contact is applied. There is some dispute in the literature about the value of D but there appears to be a correlation between poor cell performance and a silver bearing front contact which involves subsequent heat treatment.

The contact procedure presently being used is the old one. Zinc is first diffused into the aluminum-gallium arsenide in a closed ampoule. The p region is removed from the back and the back contact to the gallium arsenide is made by the evaporation of tin followed by silver and a heat treatment at 350°C for one minute. The front contact to the aluminum gallium arsenide is then made by the evaporation of silver through a mask with no subsequent heat treatment.

2. Scanning Electron Microscope Diffusion Length Measurements

Table 2 summarizes the scanning electron microscope measurements of diffusion length made for Mr. Walker and Dr. Stirn. Stirn samples of gallium arsenide-phosphide from Applied Materials Corporation, with phosphorus fractions of 0.3, were reported to have good diffusion lengths in the last report.

Measurements done in this period showed that AMC is capable of growing epi-
taxial gallium arsenide samples with diffusion lengths greater than three
microns. There is disagreement over the net electron concentration in these
samples as it is measured by our 1 MHz capacitance bridge, Stim's capacitance
technique using lower frequencies, and AMC's van der Pauw technique on separate
check layers. The AMC electron concentration measurements are usually greater
than ours and Stim's by nearly an order of magnitude.

Table 2. Summary of SEM Diffusion Length Measurements

	Material	L_p	N_D-N_A
Walker TML			
	B-4-45 top GaAs (bulk)	0.5 microns	–
	B-4-45 bottom GaAs (bulk)	1.8	–
Walker AMC			
	1772 GaAs (bulk)	0.5	$2.7 \times 10^{17} cm^{-3}$
	1944 A GaAs (bulk)	0.48	2.7×10^{17}
	1944 B GaAs (bulk)	0.51	2.7×10^{17}
	GI-18 GaAs (epi)	1.0-3.0	$1.3 \times 10^{17*}$
	GI-19 GaAs (epi)	2.4	$2.4 \times 10^{17*}$
	GI-20 GaAs (epi)	2.9-2.0	$2.6 \times 10^{17*}$
	GI-22 GaAs (epi)	3.1	$1.0 \times 10^{17*}$
Stirn AMC			
	T-245B2 GaAs (epi)	4.5	2.8×10^{15}
	T-235A7 GaAs$_{.5}$P$_{.5}$ (epi)	1.0	$1.5-1.9 \times 10^{16}$
	R-643A7 GaAs$_{.3}$P$_{.7}$ (epi)	0.42-1.0	5.8×10^{16}
	R-630A13 GaP (bulk)	0.22	1.0×10^{17}
	T-237 GaAs (epi)	4.5	4.0×10^{15}

*As measured by AMC